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9th Int. Symp. "Nanostructures: Physics and Technology"
St Petersburg, Russia, June 18–22, 2001

Epitaxial stabilization of a-PbO$_2$ structure in MnF$_2$ layers on Si and GaP

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1. Introduction

In recent years, the search for new materials for magnetic storage systems has motivated a number of studies on magnetic multilayers. This interest has been stimulated by the discovery of a giant magnetoresistance effect [1], followed by the design of spin valves [2, 3] with antiferromagnetic films playing an important role. It is well known that manganese fluoride (MnF_2) is a classical antiferromagnetic material, whose magnetic and optical properties are well understood. It was also established that it undergoes polymorphic transitions between the stable rutile-type phase in normal conditions and metastable phases having fluorite or $\alpha-PbO_2$ structures at high pressures and temperatures [4, 5]. Studies of physical properties of these metastable phases are attractive from both academic and applied points of view. While earlier studies concentrated on bulk polycrystalline systems, our efforts have been focused on MnF_2 thin films. In this connection, it is noteworthy that we have demonstrated the growth of ultrathin MnF_2 layers with the inherited cubic structure of fluorite (CaF_2) buffer on a silicon substrate [6]. In this work, we studied MBE growth and structural properties of relatively thick manganese fluoride layers on different heteroepitaxial substrates.

2. Experimental

Manganese fluoride layers were grown on Si(111), Si(001) and GaP(001) in a custom MBE system. CaF_2 or CdF_2 buffer layers were deposited before the MnF_2 growth. At high growth temperatures [7], we used CaF_2 layers to prevent a chemical interaction between MnF_2 and a Si substrate. As was found for GaP(001) substrates, CdF_2 provided the growth of large surface areas of atomic scale smooth. After standard chemical treatment [8], the silicon substrates were loaded into the growth chamber and cleaned thermally at 1250°C in an ultrahigh vacuum. This procedure produces atomically clean Si(111) surfaces with the 7×7 superstructure. The GaP(001) substrates were polished by a Br_2-isobutyl alcohol solution and washed in chloroform and acetone. Before the epitaxy, the substrates were dipped in a HF solution and fixed on Si platelets with InGa eutectic. The crystalline quality of the substrates and the growth of the buffer layers and MnF_2 films were monitored *in situ* by reflection high-energy electron diffraction (RHEED) at electron energy of 15 keV. We used a recrystallization annealing (RA) in the 550–700°C range to improve the MnF_2 film quality of some epitaxial structures grown at lower temperatures. The MnF_2 films were covered with a few CaF_2 monolayers in order to protect the grown structures from ambient humidity. X-ray diffraction measurements were carried out on a conventional DRON system with CuK_α (Ni-filter) radiation. The $\theta - 2\theta$ curves were measured in symmetrical Bragg geometry in the 2θ (6–126°) range. Side reflections were measured in a manual regime. The surface morphology measurements have been carried out in the tapping mode using a P4-SPM-MDT atomic force microscope manufactured by NT-MDT (Zelenograd, Russia).

3. Results and discussion

It was found in our previous study [9] that the surface of thick MnF_2 films grown on CaF_2/Si(111) at 400°C was relatively rough. Weak and diffused X-ray diffraction peaks prevent the identification of the film structure. In this work, we explored a low-temperature growth followed by recrystallization annealing.

The inset in Fig. 1(a) shows the RHEED pattern of a 30 nm MnF_2 film grown at 100°C and annealed at 550°C. Well-pronounced streaks indicate the single crystallinity of the film and relatively smooth surface. The AFM topography (Fig. 1(a)) demonstrates less than 10 nm of height difference on the 1×1 μm^2 square surface. There are irregular shape grains with an average size of about 100 nm. In the AFM and RHEED patterns (Fig. 1(b)), the surface roughening was observed during the further 400°C film growth on the RA surface. One can see that the height difference increases up to 60 nm with the total MnF_2 film thickness of about 100 nm. To reduce the roughness, the film growth time was divided into several stages in such a way that the growth of each 30 nm MnF_2 film at 100°C was followed by RA (at 550°C for 3 seconds). This procedure enabled growing 120–350 nm thick MnF_2 single-crystal films with a relatively smooth surface (Fig. 1(c)).

The X-ray diffraction measurements of the $\theta - 2\theta$ curves have shown the first- and second-order film peaks corresponding to $d = 0.309$ nm interplanar spacing near the intense 111 and 222 Si(111) substrate peaks. To specify the film structure, we additionally measured 19 side reflections, which unambiguously indicated that the film had 6 domains with the $\alpha-PbO_2$ structure [10]. According to [11], MnF_2 polycrystals with a metastable $\alpha-PbO_2$ phase were revealed under normal conditions just after the high-pressure drop. Following the MnF_2 film growth with RA, the MnF_2(111) planes of each domain were parallel to the Si(111) substrate, though in some cases they were rotated by $\approx 1°$ off the substrate surface, whose misorientation relative to the exact crystallographic plane did not exceed 15–20 arcmin. It was found that the lattice constants of the orthorhombic ($\alpha-PbO_2$) unit in a MnF_2 layer were $a = 0.4953$ nm, $b = 0.5798$ nm and $c = 0.5362$ nm. They are very close to the lattice constants ($a = 0.4960$ nm, $b = 0.5800$ nm, $c = 0.5359$ nm) of polycrystalline MnF_2 measured in [5]. The structural $\alpha-PbO_2$ type, like the rutile one, possesses the octahedral coordination of each Mn ion with fluorine, though the octahedron positions in the rutile and $\alpha-PbO_2$ structures are quite different. The octahedra are arranged into linear chains in the former case and into zigzag chain pattern in the latter chain [12]. The X-ray data analysis shows the following epitaxial relations: $(111)_{Si} \parallel (111)_{MnF_2}$, and $[2\bar{1}\bar{1}]_{Si} \parallel [2\bar{1}\bar{1}]_{MnF_2}$. Since conjugation of the low-symmetry ($\alpha-PbO_2$) MnF_2 phase with

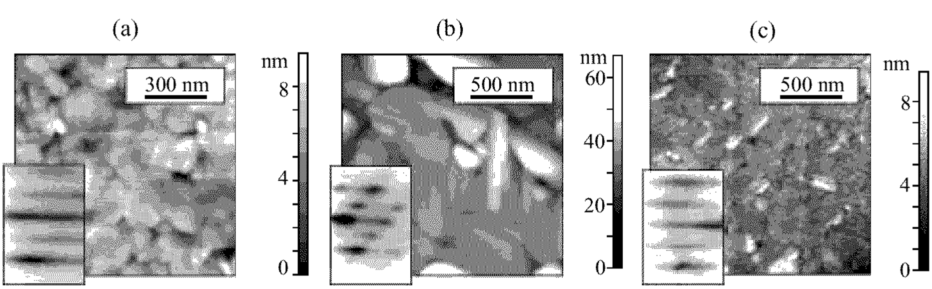

Fig. 1. AFM images and RHEED patterns (insets) of MnF_2 layers grown on Si(111) with CaF_2 buffer layer: (a) 30 nm, 20°C, RA at 550°C; (b) 85 nm, 400°C; (c) 25 nm, RA at 550°C.

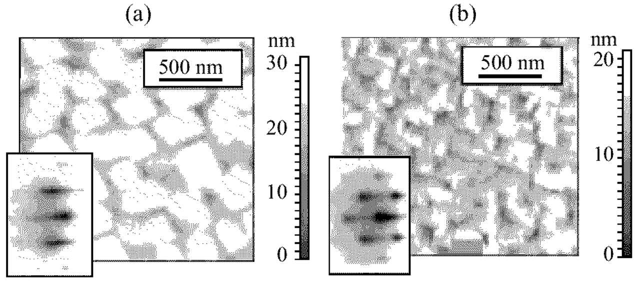

Fig. 2. AFM images and RHEED patterns (insets) of (a) 100 ml CdF_2 buffer layer on GaP(001); (b) 100 ml MnF_2, 300°C.

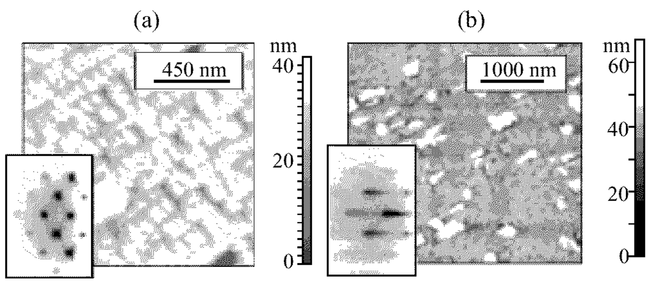

Fig. 3. AFM images and RHEED patterns (insets) of (a) 180 nm CaF_2 buffer layer on Si(001); (b) 100 nm MnF_2, 300°C, RA at 580°C.

the Si substrate takes place along high (3 m) symmetry (111) surface, it is not unexpected that the layer is formed by 120°-domains observed in the topographic images of the surface (Fig. 1(b)).

The growth of MnF_2 epitaxial films has also been studied on Si(001) and GaP(001) substrates. A smooth 100 monolayer epitaxial layer was obtained by room temperature MnF_2 deposition on a thin CaF_2 wetting layer on Si(001) [13], followed by a rapid thermal annealing at 700°C. Three well-pronounced diffraction orders of MnF_2(010) ($b = 0.580$ nm) could be seen in the $\theta - 2\theta$ curve taken from this structure in the symmetrical geometry. These peaks correspond to 020, 040 and 060 reflections in the $\alpha{-}PbO_2$ structure. Thus, the [010] direction in this film was parallel to the Si[001]. A similar epitaxial relation was found for the film grown on GaP(001) with a CdF_2 buffer layer having a large area of atomically flat (001) surface (Fig. 2(a)).

A RHEED pattern taken from the MnF_2 film grown on such a buffer is shown in the inset to Fig. 2(b). X-ray diffractometry shows that the film was mainly monocrystalline with interlayer spacing $d = 0.291$ nm. One could see (Fig. 2(b)) well-pronounced orthogonal elongated crystallites on the film, which was not unexpected for orthorhombic structure of the layer. The growth of MnF_2 layers on a relatively thick CaF_2 buffer layer on Si(001) at 300–600°C provided a facetted surface. Bright spots at intersections of inclined streaks in the RHEED pattern (inset to Fig. 3(a))were due to the fluorite islands with {111} facets (Fig. 3(a)). After the beginning of the MnF_2 growth, diffused spots appeared. Further growth resulted in their elongation normal to the surface, indicating the surface flattening. Annealing of the grown structure at 580°C improved its crystallinity and planarity

(Fig. 3(b)). The X-ray diffraction $\theta - 2\theta$ curve taken from this film showed only 200 and 400 reflections of the orthorhombic structure. This indicates that the [100] film direction was aligned with the [001] substrate direction.

4. Summary

Epitaxial MnF_2 films as thick as 350 nm have been grown on Si and GaP substrates. X-ray diffractometry revealed that the MnF_2 films have the $\alpha-PbO_2$-type orthorhombic structure with the lattice parameters $a = 0.4953$ nm, $b = 0.5798$ nm, $c = 0.5362$ nm. It was found that the films grown on Si(111) have $(111)_{Si} \| [2\overline{1}\overline{1}]_{MnF_2}$ and $[2\overline{1}\overline{1}]_{Si} \| [2\overline{1}\overline{1}]_{MnF_2}$ orientations. These epitaxial relations agree with three crystallite orientations observed by AFM. Manganese fluoride films grown on Si(001) had the same orthorhombic structure, however $[010]_{MnF_2}$ or $[100]_{MnF_2}$ were directed along the surface normal, depending on the surface morphology of the buffer layer. Optical and magnetic measurements of the MnF_2 layers are underway.

Acknowledgements

This work was supported by grants of Russian Ministry of Sciences (No 99-2043) and Swiss National Science foundation (No 7SUPJ062359).

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